ELSEVIER

Polymer 43 (2002) 4605–4610

polymer

www.elsevier.com/locate/polymer

Interphase formation in model composites studied by micro-thermal analysis

G. Van Assche, B. Van Mele*

Department of Physical Chemistry and Polymer Science, Free University of Brussels, Pleinlaan 2, B-1050 Brussels, Belgium

Received 19 November 2001; accepted 26 April 2002

Abstract

Micro-thermal analysis was used for studying interphases formed in particle-filled composites based on an epoxy resin matrix. The subsurface distribution of the particles can be observed in the conductivity images, while spatial variations in thermal properties can be determined by local thermal analyses.

For an anhydride-cured epoxy system filled with porous silica particles, an interphase is observed around the particles. In the ca. 60 μm wide interphase, the glass transition temperature gradually decreases from the bulk value to a value about 10 °C lower. The less densely cross-linked interphase can be detected in the thermal conductivity images and in the local thermal analyses. The interphase formation is attributed to the effect of adsorbed water on the polymerisation mechanism. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Micro-thermal analysis; Modulated temperature differential scanning calorimetry; Interphase

---

1. Introduction

The macroscopic properties of composite materials, including fibre-reinforced polymers, blends, and multi-layer systems, are often strongly affected by the development of interphase regions with properties differing from the properties of the constituent materials. Interphases can arise due to preferential adsorption, catalytic influences of a surface, inter-diffusion, phase separation, etc. The resulting gradients in composition (polymer blends) or crosslink density (thermosets) lead to gradients in the microscopic properties.

Using thermal analysis techniques, average macroscopic properties of the multiphase materials can be determined as a function of time and temperature, e.g. the heat capacity (differential scanning calorimetry or DSC, and modulated temperature differential scanning calorimetry or MTDSC[1]), the thermal expansion coefficient (thermomechanical analysis or TMA), and the modulus of elasticity or viscoelastic character (dynamic mechanical analysis or DMA). The phase morphology, surface topology and some (local) information about the constituent phases can be obtained by different types of microscopy.

Micro-thermal analysis (micro-TA) combines the advantages of both thermal analysis (characterisation) and microscopy (visualisation). First, surface images are obtained by mapping the topology and thermal properties in a way similar to scanning thermal microscopy (SThM). Subsequently a characterisation is made on a micrometer scale by raising the temperature of the probe tip and following the response while keeping it at a certain selected location (localised thermal analysis or L-TA mode). Thus, micro-TA allows one to study spatial variations in glass transition and melting behaviour by performing local thermal analyses on micrometer-scale areas. A comprehensive discussion of this technique and its applications can be found in a review by Pollock and Hammiche [1] and references therein.

In this paper, micro-TA is used for the micro-characterisation of an interphase in a composite material based on a thermosetting epoxy system. Häßler and zur Mühlen [2] presented results for interfaces formed in two epoxy-based composites: an epoxy cured in contact with an anodised aluminium sheet, and one cured in the presence of coated fibres. Both systems showed an increase of the glass transition temperature close to the solid surface. The origin of this increase was not clarified. This paper focuses on

---

* Corresponding author. Tel.: +32-2-6293276; fax: +32-2-6293278. *E-mail address:* bvmele@vub.ac.be (B. Van Mele).

[1] Other commonly used acronyms for this technique are MDSC™, TMDSC, and DSTMC.

PII: S0032-3861(02)00298-7

particle-reinforced epoxy systems based on two different hardeners.

2. Experimental

2.1. Materials

Particle-based composite samples were made by combining an epoxy resin with glass or silica particles.

The bifunctional DGEBA-type epoxy resin (Epikote 828 VLEL, Shell) was cured using an amine or an anhydride hardener. The amine-cured epoxy system is a stoichiometric mixture of the epoxy with MDA (4,4′-methylenedianiline, Aldrich). For the anhydride-cured epoxy, the epoxy was mixed with an anhydride hardener (methyltetrahydrophthalic anhydride, HY917, Ciba-Geigy) and an accelerator (1-methyl imidazole, DY070, Ciba-Geigy) in a 100/87.4/1 weight ratio. These epoxy systems were combined with 10% (w/w) of either small glass spheres (diameter < 80 μm) or porous silicate particles (diameter ca. 150 μm). All materials were used without any pre-treatment. The porous silica particles contain ca. 5% (w/w) of water (determined by TGA). For comparison, composites were also prepared with dried silica particles, which due to their hygroscopic nature still contain 2.5% of water (determined by TGA).

Samples for micro-thermal analysis were prepared by curing the (filled) resins between glass slides. An isothermal cure at 80 °C for 300 min was followed by heating to 175 °C at 20 °C min^{-1}, and a post-cure for 5 min at 175 °C. After curing, one of the glass slides was removed and the exposed surface was studied without any further treatment.

2.2. Instruments

2.2.1. Micro-thermal analysis (micro-TA)

To study the composite surfaces, a TA-instruments μTA™ 2990 micro-thermal analyser was used. The instrument was calibrated using room temperature and the DSC peak melting points of commercial poly(ethylene oxide) (PEO), polyethyleneterephthalate (PET), and polyetheretherketone (PEEK). Within the experimental error a linear calibration curve was obtained. Two modes of micro-TA measurements were used. In a *surface mapping* the thermal probe is scanned in AFM-contact mode over a 100 μm × 100 μm (or smaller) area. A contact force corresponding to ca. 10 nA was used. The probe was held at a temperature of 100 °C with a 30 kHz modulation of 5 °C amplitude superimposed. This results in images of the topography, the thermal conductivity, and the amplitude and phase difference of the sample response to the superimposed temperature modulation.

In a second step, *localised thermal analysis* (L-TA) measurements were made. The probe is held in contact at a location selected in the *mapping*. The temperature of the probe is raised from 25 to 275 °C and cooled to 25 °C at 20 °C s^{-1}. The following signals are measured: (1) the vertical position of the probe (L-TMA, localised thermomechanical analysis, or sensor signal), (2) the power difference between sample and reference probe (L-CA, localised calorimetry, or power signal), and (3) the amplitude and phase difference of the sample response to the superimposed temperature modulation (L-MTDTA, localised modulated temperature differential thermal analysis). A measurement in the air was used as a baseline signal. For the experimental conditions used, the signal-to-noise ratio was worse for the L-MDTA signals. Therefore, these signals will not be discussed here.

2.2.2. Modulated temperature differential scanning calorimetry (MTDSC)

MTDSC was used to study the cure and vitrification behaviour, and to determine the final glass transitions of filled and unfilled resins. Measurements were made in hermetic aluminium pans on a TA Instruments 2920 DSC with MDSC™ option and equipped with a RCS. The instrument was calibrated for temperature using indium and cyclohexane, for enthalpy using indium, and for the heat capacity using polymethylmethacrylate. The glass transition temperatures were measured at an underlying heating rate of 2.5 °C min^{-1}. A 1 °C per 60 s modulation was superimposed.

3. Results and discussion

3.1. Cure and vitrification by MTDSC

The cure and vitrification behaviour of the model epoxy composites was studied by MTDSC, a technique that has proven its strength for studying reacting polymer systems [3–7]. Filled and unfilled epoxy resins were cured quasi-isothermally at 90 °C for 300 min. The residual cure and the final glass transition were determined in subsequent cool–heat cycles at 2.5 °C min^{-1}. The isothermal cure results for the anhydride-cured epoxy are given in Fig. 1. The rate of the autocatalytic cure reaction, observed as an exotherm in the non-reversing heat flow, is only slightly influenced by the filler. Although the reaction kinetics are not much influenced, the vitrification of the resin, seen as a decrease in heat capacity [3,5,6], is clearly delayed for the silica-filled resins.

The final glass transition T_g of the (wet) silica-filled resin is about 18 °C lower than for the unfilled resin (Fig. 2). For dried silica particles (still 2.5% water adsorbed), the glass transition lies in between the transition for neat resin and for resin with (wet) silica particles, which indicates that the water adsorbed on the particles causes the decrease in T_g. In accordance, the curves for the glass-filled resin nearly coincide with those for the unfilled resin. The evolution of the temperature-derivative of the heat capacity shows that the transition is also wider for particles with more moisture.

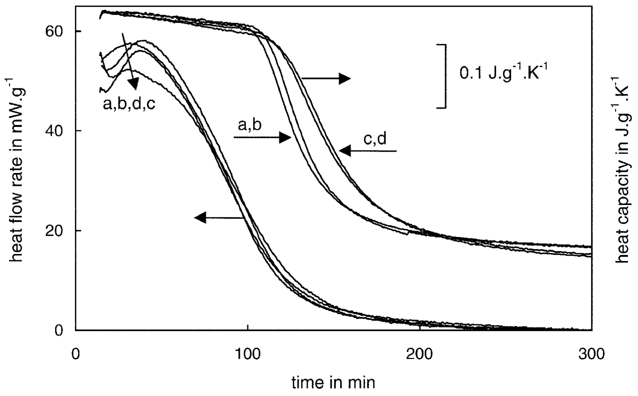

Fig. 1. Heat flow and heat capacity for the isothermal cure of filled and unfilled anhydride-cured epoxy resins at 90 °C. (a) Unfilled, (b) 10% glass, (c) 10% silica, (d) 10% dried silica. Obtained by MTDSC.

Moreover, for the (wet) silica particles a bimodal distribution is observed (see Fig. 2, dC_p/dT, curve C). The bimodal nature (or the increased width of the transition) points to a wider distribution in crosslink densities and is a macroscopic indication for the presence of an interphase in this epoxy-anhydride/silica composite. For composites with an amine-cured epoxy matrix, the glass transition was not significantly influenced by the presence of glass or silica particles.

3.2. Detection of an interphase by micro-TA

To study the interphase on a microscopic level, *micro-TA* was employed. In a first step, the surface is mapped for topography and thermal properties. Results for an anhydride-cured epoxy filled with glass beads are given in Fig. 3. The glass particles can be observed in the three images. In the topography mapping, circular patterns of about 20 μm diameter are observed. The height of these patterns (less than 300 nm) is much less than the size of the particles (about 80 μm). This indicates that the particles are really embedded in the matrix and covered by resin (Fig. 4). The ring-like pattern observed is probably caused by cure-induced shrinkage of the resin around the solid particles. In the thermal conductivity mapping, the particles are observed as zones with a higher value. This agrees with a ca. four times higher bulk thermal conductivity and diffusivity for the glass as compared to the values for epoxy resins. As the probe moves away from the (projected) centre of a particle, the amount of resin in the analysed volume will increase and the thermal properties, averaged over the analysed volume, gradually decrease to a lower level corresponding to the resin (Fig. 4).

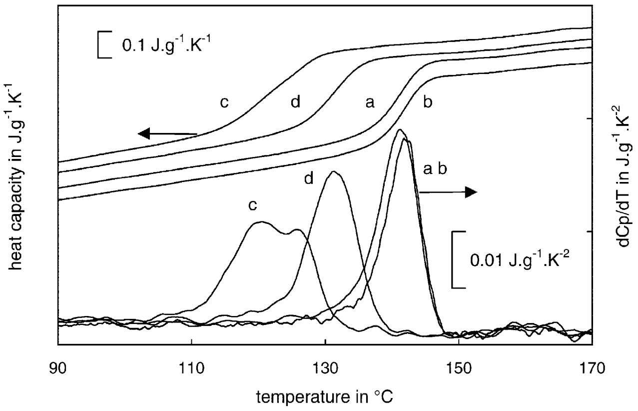

Fig. 2. Heat capacity and derivative vs. temperature for the final glass transition for filled and unfilled anhydride-cured epoxy resins. (a) Unfilled, (b) 10% glass, (c) 10% silica, (d) 10% dried silica. Obtained by MTDSC in second heating.

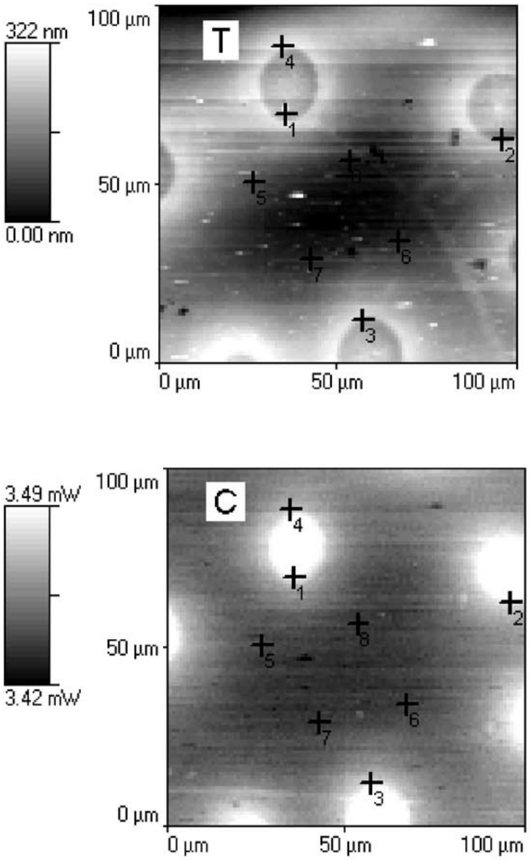

Fig. 3. Topography (T) and conductivity (C) images from a micro-TA-mapping for an anhydride-cured epoxy system filled with glass beads. Locations selected for L-TA measurements are indicated.

On the 2D-mappings, positions can be selected, as indicated in Fig. 3. In these positions L-TA (local thermal analysis) was performed by raising the temperature of the thermal probe at 20 °C s^{-1} to 275 °C. A typical L-TA result is shown in Fig. 5. The onset of the penetration of the probe, observed in the L-TMA signal, can be used as a relative measure for the local glass transition of the matrix. Alternatively, the derivative of the L-TMA signal and the derivative of the L-CA signal can be used to characterise the transition. For these highly cross-linked thermoset resins, the modulated signals (L-MDTA) did not give reproducible results.

To detect and characterise an interphase surrounding the particles, L-TA measurements were made in positions

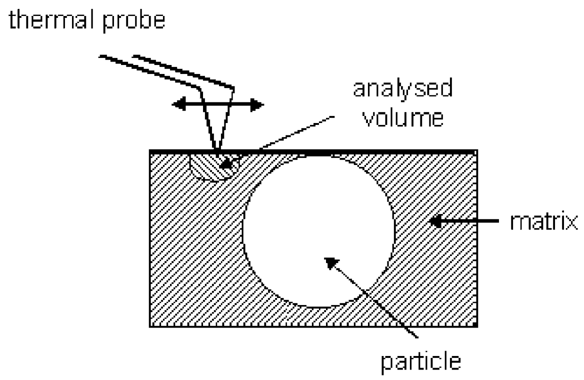

Fig. 4. Schematic drawing showing the micro-TA mapping of a thermoset matrix with a particle embedded. As the probe moves over the particle, the contribution of the particle to the analysed volume gradually changes.

further away from and closer to the (projected) centre of the particle. For the silica and glass-filled epoxy-amine systems and for the glass-filled epoxy-anhydride, the influence of the distance to the particle is less than the scatter on the measurements (Table 1). Although there is no significant difference in glass transition between locations closer to and further away from the particle, the trend is to have a slightly higher glass transition closer to the particle. This might be related to a restricted mobility closer to the particle surface.

For the composites based on silica particles, the particles are observed as a zone with a lower thermal conductivity than the surrounding matrix (Fig. 6). This can be attributed to a lower thermal conductivity of the porous silica. For the silica-filled epoxy-anhydride system, the system for which indications for an interphase were found in MTDSC, a large zone is observed in which the conductivity slowly evolves to the value for the bulk of the matrix. This gradual evolution extends over 60–80 μm, as confirmed by the line-scan (Fig. 7). To determine the origin of this thermal conductivity gradient, L-TA measurements were made in positions on lines radiating from the (projected) centre of the particle (Fig. 6). In the bulk of the material, sufficiently far from the particle, the glass transition temperature is constant. As the distance to the (projected) centre of the particle decreases, the glass transition decreases 10–15 °C over 60–80 μm (Fig. 8). The distance over which this decreasing T_g stretches (in L-TA) is comparable to the distance over which the gradual evolution in thermal conductivity is observed in the surface mappings (Figs. 1 and 7). Although the results show a considerable scatter, the trend is clear and reproducible for all different quantification approaches used. Thus, an interphase with a decreased T_g (compared to the bulk value) is surrounding the silica particles. This is in agreement with the decreased and wider macroscopic T_g for the silica-filled anhydride-cured epoxy resin, as observed by MTDSC.

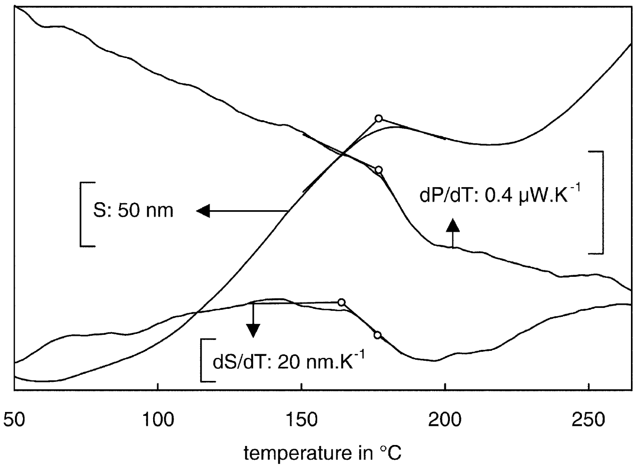

Fig. 5. L-TA measurement of the local softening point for an epoxy-anhydride filled with glass beads (location 1 in Fig. 3). L-TMA signal (S), and temperature derivatives of L-TMA (dS/dT) and L-CA (dP/dT) signals.

Table 1
L-TA results for local softening point (°C) of an amine-cured epoxy resin filled with glass beads for locations close to and further away from the particles (Fig. 3). Average and standard deviation for onset in L-TMA signal (S), for temperature at half height and maximum in the derivative L-TMA signal (dS/dT), and for onset of stepwise decrease in the derivative L-CA signal (dP/dT) (Fig. 5)

	Signal	S onset	dS/dT		dP/dT
Position			1/2 h	Max.	Onset
Close	Average	171.1	172.4	196.6	173.4
	Standard deviation	4.2	4.8	4.7	4.0
Further	Average	170.1	171.6	195.1	173.4
	Standard deviation	3.1	4.7	1.1	2.1

The decrease in T_g as we move closer to the particle surface points to a decrease in crosslink density. This lower crosslink density is expected to lead to a lower thermal conductivity. Indeed, the thermal conductivity increases with advancing network formation [8], which can be attributed to a faster thermal conduction along the chains than between the chains and to an increasing density [9]. In conclusion, interphases with a gradient in crosslink density can be detected in both L-TA and surface mapping measurement modes.

3.3. Polymerisation mechanism and interphase formation

The zone with a reduced crosslink density that surrounds the silica particles in anhydride-cured epoxy resin can be attributed to the influence of adsorbed water on the epoxy-anhydride network formation. The porous silica particles have a large specific area on which water easily adsorbs; ca. 5% of water is present on the silica particles used (determined by TGA). During the mixing of the particles in the resin and during the cure procedure, water will diffuse into the reacting matrix. For the anionic polymerisation of an epoxy-anhydride system catalysed with a tertiary amine, water participates in the cure chemistry through termination reactions [10]. Similar termination reactions are known to cause the poisoning effect of water on anionic polymeris-

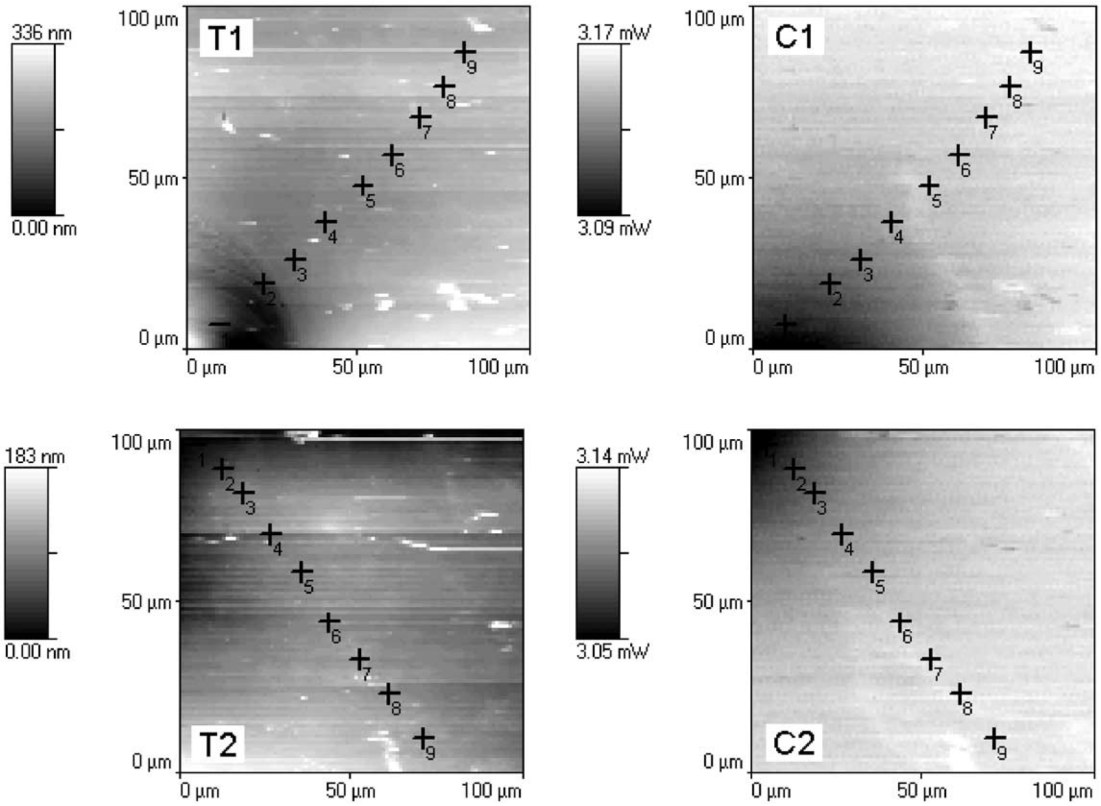

Fig. 6. Micro-TA topography (T) and conductivity (C) images from mapping in 2 positions (1 and 2) for an epoxy-anhydride filled with silica particles. Selected locations for L-TA measurements are indicated (crosses).

ation reactions. Thus, in case of the catalysed epoxy-anhydride network formation, the presence of water results in a less densely cross-linked network with a lower glass transition [11]. In contrast, the step-growth addition reaction of an epoxy with an amine is accelerated by water, but the network formation is not influenced.

The diffusion of the water from the particles into the (reacting) matrix will determine the thickness and properties of the interphase. It is worth noting in Fig. 2 that for the anhydride-cured epoxy with silica filler two effects can be distinguished. First, the 'average' glass transition of the matrix is considerably lowered, and second, a bimodal distribution develops. This can be attributed to water diffusing from the silica particles into the matrix in two stages. At first, while dispersing the filler into the resin at

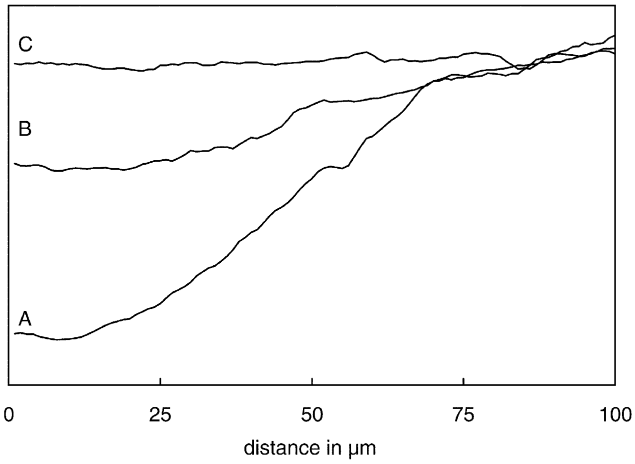

Fig. 7. Line scans of a micro-TA conductivity image for an epoxy-anhydride filled with silica particles (Fig. 6, C1). Y-displacement of line scan with respect to origin: (A) 0 µm, (B) 68 µm, (C) 100 µm.

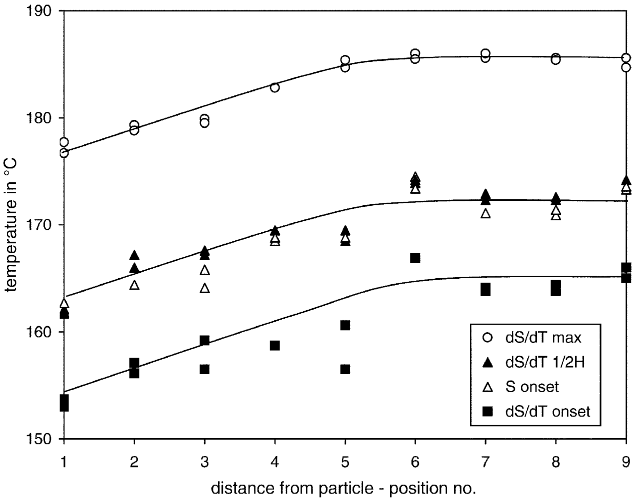

Fig. 8. L-TA results for local softening of an epoxy-anhydride filled with silica particles. Distance from particle increases about 10 µm with increasing position number. Results for two lines of positions radiating from the same centre (Fig. 1). L-TMA signal (S) and temperature derivative of L-TMA (dS/dT). Solid lines are sketched evolutions.

room temperature (reaction very slow), part of the adsorbed water diffuses into the matrix. This water will be distributed evenly into the matrix. Upon curing the composite at a more elevated temperature, this water will terminate the cross-linking polymerisation, reduce the 'average' glass transition of the system, and cause a slower vitrification.

Secondly, when the temperature is raised to cure the composite, water still present in the particles might diffuse into the reacting matrix, and participate in the termination reactions. The changing balance between the rate of diffusion and the rate with which the water molecules are captured in the termination reactions will determine the distance that these water molecules diffuse into the polymerising matrix. Thus, the water diffusing from the particles into the matrix during the cure would cause the formation of the interphase with a lowered cross-linking density compared to the (decreased) bulk value, creating a bimodal distribution in the overall glass transition of the composite.

4. Conclusion

Micro-TA was used for studying the presence and properties of interphases in particle-filled composites based on an epoxy resin cured with different hardeners. Using the 2D-mapping, the distribution of the particles can be observed, while spatial variations in thermal properties can be determined in local thermal analyses.

For an anhydride-cured epoxy system filled with porous silica particles, an interphase with lower T_g surrounds the silica particles. This interphase can be attributed to the effect of water that is adsorbed on the silica surface: it diffuses into the curing matrix and reduces the cross-link density. The resulting interphase with a decreased glass transition can be detected in both the thermal conductivity surface mappings and in the local thermal analyses.

Acknowledgment

G. Van Assche is a postdoctoral researcher of the Foundation for Scientific Research—Flanders (Belgium).

References

[1] Pollock HM, Hammiche A. J Phys D 2001;34:R23–R53.

[2] Häßler R, zur Mühlen E. Thermochim Acta 2000;1–2:113–20.

[3] Van Assche G, Van Hemelrijck A, Rahier H, Van Mele B. Thermochim Acta 1995;268:121–42.

[4] Van Assche G, Van Hemelrijck A, Rahier H, Van Mele B. Thermochim Acta 1996;286:209–24.

[5] Van Assche G, Van Hemelrijck A, Rahier H, Van Mele B. Thermochim Acta 1997;305:317–34.

[6] Swier S, Van Assche G, Van Hemelrijck A, Rahier H, Verdonck E, Van Mele B. J Therm Anal Cal 1998;54(2):585–604.

[7] Van Assche G, Verdonck E, Van Mele B. Polymer 2001;42(7): 2959–68.

[8] Pusatcioglu SY, Fricke AL, Hassler JC. J Appl Polym Sci 1979;24: 947–52.

[9] Godovsky YK. Thermophysical properties of polymers. Berlin: Springer; 1992. p. 57–60.

[10] Steinmann B. J Appl Polym Sci 1990;39:2005–26.

[11] Van Mele B, Verdonck E. J Adhes 1996;57:245–60.